

# Adsorption–Desorption of 2,4-D by Hydroxy Aluminium Montmorillonite Complexes\*

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**Abstract:** Adsorption–desorption characteristics of 2,4-dichlorophenoxyacetic acid (2,4-D) on pure montmorillonite and synthetic chlorite-like complexes  $[\text{Al}(\text{OH})_x\text{-montmorillonite}]$  were investigated. The equilibrium adsorption of 2,4-D was described by both Langmuir and Freundlich type isotherms. The extent of adsorption as well as the type of interaction between adsorbate and adsorbent was affected by the nature of incubation buffer and the charge characteristics of supports. At pH 5.6 and in acetate buffer, 2,4-D was negatively adsorbed by montmorillonite and herbicide adsorption capacity increased with increasing amounts of  $\text{Al}(\text{OH})_x$  species loaded on montmorillonite surfaces. When adsorption experiments were performed at the same pH but in phosphate buffer, strong reductions of both the amount of adsorbed pesticide and its affinity for the adsorbents were measured. Evidently, phosphate anions competed strongly with 2,4-D anions for the sorption site on chlorite-like complexes. Furthermore, desorption tests revealed that a large amount (about 60%) of the pesticide was firmly bound to the clay and was not removed even after repeated washings or 24 h exposure to desorption solution. Both electrostatic interactions between the negative  $\text{COO}^-$  moieties of 2,4-D and the positive sites on clays, and ligand exchanges of  $\text{COO}^-$  groups with  $-\text{OH}$  or water at the clay surface were probably involved in the adsorption process.

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## 1 INTRODUCTION

Adsorption is one of the key processes affecting the ultimate fate of pesticides in soils. In particular, the interactions at the interface between organic and inorganic soil colloids and pesticides through adsorption–desorption mechanisms may influence movement of pesticides, and thus their availability for plant or microbial uptake, or their transformation by abiotic or biotic

agents. The extent of adsorption is related to various soil properties, including organic matter content, type and content of clay, exchange capacity, acidity,<sup>1,2</sup> and to physical and chemical parameters of the adsorbed compound.

Organo-mineral complexes appear to be the soil components mainly involved in the interaction with pesticides. Therefore, they could be regarded as a tool to decrease the contamination of soils and waters.<sup>3,4</sup> A predominant role in the complex associations between organic matter and clay minerals is played by monomers, polymers and non-crystalline precipitation products of aluminium. These aluminium products facilitate the adsorption of organic molecules on the clay surfaces.<sup>5</sup> Many investigations have been carried out on the adsorption of pesticides to clays,<sup>6,7</sup> oxide

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minerals,<sup>8,9</sup> humic substances,<sup>10</sup> and to various soils.<sup>11,12</sup> However, less information is available on the adsorption-desorption of pesticides on 'dirty clays', i.e. clay minerals coated, partially or completely, with polymeric species or non-crystalline oxides of aluminium and iron, in spite of the fact that these minerals predominate in acidic soil environments.<sup>13</sup> In particular, the coating of pure phyllosilicates with  $\text{Al}(\text{OH})_x$  species (to simulate the 'dirty clays') strongly modifies their physicochemical properties, thus influencing the interaction between nutrients, organics and the phyllosilicates.

In soil weathering processes, expansible layer silicates, vermiculites and smectites, which are negatively charged, adsorb positively charged monomers and polymers as well as non-crystalline precipitates of aluminium to form hydroxy-interlayered minerals. These minerals occur in soils throughout the world and are present in soils of several orders. However, they are particularly abundant in the Ultisols and the Alfisols. Interlayering is greatest in the surface horizon and decreases with depth.<sup>14</sup>

The objective of this work was to study the adsorption/desorption processes of the weakly acidic herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) on a montmorillonite (clean clay), and on chlorite-like complexes  $[\text{Al}(\text{OH})_x\text{-montmorillonite}]$ , obtained by coating montmorillonite surfaces with different amounts of  $\text{Al}(\text{OH})_x$  species. 2,4-D is an aquatic and systemic herbicide widely used on wheat, corn and sorghum to control broad-leaf weeds and is a potential pollutant of ground waters. It was chosen as a model of anionic organic pollutants and because it was one of chemicals used by European Commission for the ring-test on adsorption-desorption of chemicals in soils.

## 2 EXPERIMENTAL METHODS

### 2.1 Clay minerals

The  $<2\text{-}\mu\text{m}$  fraction of Na-saturated montmorillonite (M) from Crook, USA was washed with water and dialysed until free from chloride ions. The Na-montmorillonite was freeze-dried and stored at room temperature. A sample of clay was further purified by eliminating any organic or inorganic impurity, according to the method of Jackson.<sup>15</sup>

The  $\text{Al}(\text{OH})_x\text{-montmorillonite}$  complexes (AM) were obtained by adding 0.1 M NaOH to a mixture of  $\text{AlCl}_3$  and montmorillonite suspension, containing 3, 9 or 18 milli-equivalents of aluminium  $\text{g}^{-1}$  clay ( $\text{AM}_3$ ,  $\text{AM}_9$  and  $\text{AM}_{18}$ , respectively). The addition of NaOH was stopped when the mixture reached pH 6.5. The suspension was washed until free of chloride and then freeze-dried. The chemical and physicochemical properties of the clay minerals are given in Table 1.

**TABLE 1**  
Chemical and Physicochemical Properties of Clay Minerals

Clay <sup>a</sup>	Cation exchange capacity (meq 100 g <sup>-1</sup> )	d001 (nm)	Surface area (m <sup>2</sup> g <sup>-1</sup> )
M	59.08	1.170	812
AM <sub>3</sub>	53.20	1.280	628
AM <sub>9</sub>	25.10	1.470	315
AM <sub>18</sub>	16.00	1.508	180

<sup>a</sup> For details see Section 2.1.

The cation-exchange capacity (CEC) of the complexes was determined by the  $\text{BaCl}_2\text{-TEA}$  method<sup>16</sup> and the surface area of the clay minerals by the ethylene glycol monoethyl ether (EGME) gravimetric method.<sup>17</sup> Oriented aggregate specimens of the K-saturated samples for X-ray diffraction (XRD) were obtained by drying aliquots of samples on glass slides. XRD patterns were obtained with a Rigaku diffractometer with  $\text{Co-K}_\alpha$  radiation generated at 40 kV and 30 mA.

### 2.2 Chemicals

2,4-Dichlorophenoxyacetic acid (2,4-D; 99.6% purity) was purchased from Dr Ehrenstorfer GmbH (Germany). HPLC solvents were from Lab Scan, Ireland. All other chemicals, (analytical grade), were from Serva GmbH (Germany).

### 2.3 Experimental conditions

Mixtures containing 2,4-D (10–100  $\mu\text{g ml}^{-1}$ ) and clay (50 mg) in a final volume of 2.5 ml (solid/liquid ratio of 20) were shaken at 25°C for 24 h. Buffered clay suspensions were sonicated for 10 min before pesticide addition. These incubation tests were performed in acetate and phosphate buffer at pH 5.6 (both at 0.01 M). After incubation, the suspensions were centrifuged (10 000g; 15 min) using a Sorvall SS34 Rotor in a Sorvall RC-5B Refrigerated Superspeed Centrifuge. The amount of residual 2,4-D in the supernatant was analysed by HPLC.

The HPLC analyses were carried out with a Varian apparatus, equipped with a Varian Mat pump, and vari-Chrom variable wavelength absorbance detector set at 280 nm. A Speri-5-RP18 22 cm  $\times$  4.6 mm C18-80 column (BrownLee) of 5  $\mu\text{m}$  particle size was utilised; isocratic elution was performed at a flow rate of 1.8 ml min<sup>-1</sup> with acetonitrile + phosphate buffer (0.04 M, pH 2.95; 35 + 65 by volume) as mobile phase.<sup>18</sup>

Adsorption isotherms were obtained by plotting the amount of herbicide adsorbed on clays (calculated by the difference between the initial and final concentration of the herbicide in solution) versus equilibrium pesticide

concentration. The sorption data were analysed according to the Langmuir and Freundlich equations.

The Langmuir equation can be written as follows:

$$x = x_m kc / (1 + kc) \quad (1)$$

where  $x$  is the amount of pesticide adsorbed per unit weight of the clay ( $\mu\text{g g}^{-1}$ ),  $k$  is a constant related to the binding energy ( $\text{ml } \mu\text{g}^{-1}$ ),  $x_m$  is the maximum amount of pesticide adsorbed ( $\mu\text{g g}^{-1}$ ) and  $c$  is the equilibrium concentration of the pesticide ( $\mu\text{g ml}^{-1}$ ).

The Freundlich equation is:

$$x = Kc^{1/n} \quad (2)$$

where  $x$  and  $c$  are defined in eqn (1), and  $K$  and  $n$  are constants that give estimates of the adsorptive capacity and intensity, respectively.

At saturation levels, the values of distribution coefficient  $K_d$  (defined as the ratio of the concentration of pesticide adsorbed per unit weight of the clay to its equilibrium concentration;  $\text{ml g}^{-1}$ ) were also determined.

Desorption tests were performed by replacing with equal volumes of buffer or  $\text{CaCl}_2$  (0.01 M) solutions the supernatants collected after incubation of the clay-pesticide mixtures for 24 h at 25°C. The pesticide desorption was evaluated as function of contact time and washing numbers.

All experimental tests were conducted at least in triplicate and the relative standard deviation ranged from 0 to 4%.

### 3 RESULTS

#### 3.1 Properties of clay minerals

Some chemical and physicochemical properties of samples are summarised in Table 1. The cation exchange capacity (CEC) and the surface area of samples decreased from 59.08 to 16 meq 100  $\text{g}^{-1}$  and from 812  $\text{m}^2 \text{g}^{-1}$  to 180  $\text{m}^2 \text{g}^{-1}$  by increasing  $\text{Al}(\text{OH})_x$  species sorbed on montmorillonite surfaces, clearly because of the greater interlayering of  $\text{Al}(\text{OH})_x$  ions in the complexes containing higher amounts of aluminium. In fact, X-ray diffraction (XRD) analysis showed  $d$ -spacings of 1.170 nm for Na-montmorillonite, and of 1.280, 1.470 and 1.508 nm for  $\text{AM}_3$ ,  $\text{AM}_9$  and  $\text{AM}_{18}$ , respectively.

#### 3.2 Adsorption studies

Preliminary experiments were conducted to choose the experimental conditions most suitable for the adsorption of 2,4-D on clays. Experiments were performed by changing the solid/liquid ratio, the nature of the buffer and the pH. When experiments were carried out in

water, no detectable adsorption was observed at pH 5, 6 or 7, achieved by addition of hydrochloric acid or sodium hydroxide. On the contrary, a measurable amount of 2,4-D was held on clays at pH 5-6, incubated in acetate or phosphate buffer. These results refer to a solid/liquid ratio of 20. In fact, solid/liquid ratios of 1.5, 2.5, 5 and 10 failed to give any measurable 2,4-D adsorption. A solid/liquid ratio of 20, a pH of 5-6 and acetate and phosphate buffers were chosen for the experiments discussed in the following sections.

Kinetic runs established the time needed to reach adsorption equilibrium. The experiments were performed with  $\text{AM}_{18}$  in 0.01 M acetate buffer at pH 5-6. Adsorption equilibrium was reached within 20 h (Fig. 1) and no detectable modification in the adsorbed amount took place after this period. Initially 2,4-D adsorption was very fast, then continued slowly, reaching the maximum after 24 h of contact time. Similar behaviour was obtained with the other clays (data not shown). A mixing period of 24 h was then adopted to ensure that equilibrium was attained.

In acetate buffer, no significant adsorption occurs on montmorillonite, according to results reported by several authors.<sup>7,19-21</sup> On the other hand, increasingly greater amounts of 2,4-D were adsorbed on clays coated with increasing amounts of  $\text{Al}(\text{OH})_x$  species on montmorillonite surfaces (Fig. 2).

The adsorption isotherms for 2,4-D at 25°C and pH 5-6 in 0.01 M acetate buffer with  $\text{AM}_3$ ,  $\text{AM}_9$  and  $\text{AM}_{18}$

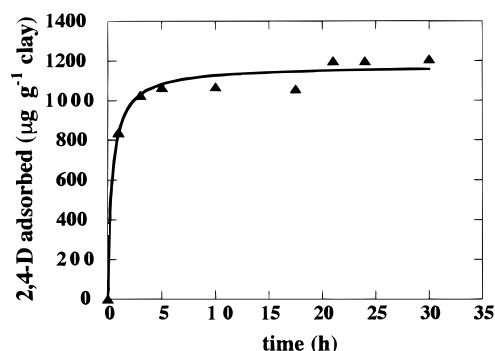


Fig. 1. Kinetics of adsorption of 2,4-D on  $\text{AM}_{18}$  at 25°C and pH 5-6 in 0.01 M acetate buffer.

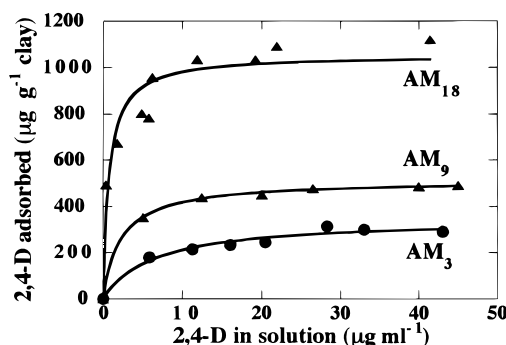


Fig. 2. Adsorption isotherms of 2,4-D at 25°C and pH 5-6 in 0.01 M acetate buffer on  $\text{Al}(\text{OH})_x$ -montmorillonite complexes.

complexes (Fig. 2) fitted the Langmuir equation (determination coefficients  $r^2 > 0.90$ ). The best-fitting curves through the experimental data were calculated by a computed non-linear regression analysis, according to the Langmuir equation by the least-squares method. The shapes of the isotherms were different and were distinguished by the initial slope. The adsorption of 2,4-D on  $AM_3$  and  $AM_9$  increased more slowly with increasing herbicide equilibrium concentration and the Langmuir isotherm approximated the L-form.<sup>22</sup> By contrast, the shape of the curve for  $AM_{18}$  suggests a high-affinity behaviour,<sup>22</sup> the adsorption being characterised by a rapid rise at low herbicide equilibrium concentrations. The data also fitted the Freundlich equation, as supported by the high values of  $r^2$  (Table 2). The values of Langmuir and Freundlich constants  $k$  and  $n$  indicated that  $AM_{18}$  adsorbed 2,4-D with both the greatest binding energy and sorptive intensity (Table 2). The amount of 2,4-D adsorbed on clays followed the order  $AM_{18} > AM_9 > AM_3$ . At a  $20 \mu\text{g ml}^{-1}$  equilibrium concentration of 2,4-D, the amount of adsorbed herbicide significantly increased from 220 on  $AM_3$  to 466 and  $1018 \mu\text{g g}^{-1}$  clay on  $AM_9$  and  $AM_{18}$ , respectively. This trend was also confirmed by the distribution coefficients  $K_d$ , which linearly increased with increasing amount of  $Al(OH)_x$  species held on montmorillonite surfaces (Table 2).

When adsorption experiments were carried out at the same pH but in phosphate buffer, a different behaviour was observed. A lower adsorption occurred on chlorite-like complexes and, surprisingly, pure montmorillonite adsorbed 2,4-D at appreciable levels.

Figure 3 shows the adsorption isotherms at  $25^\circ\text{C}$  and pH 5.6 in 0.01 M phosphate buffer of 2,4-D on M and  $AM_{18}$  complex. The experimental data were analysed by a computed non-linear regression analysis, according to the Langmuir equation by the least-squares method. As shown in the figures, at the saturation level, about 600 and  $300 \mu\text{g g}^{-1}$  clay of 2,4-D were adsorbed by montmorillonite and  $AM_{18}$ , respectively. In particular, when the adsorption occurred on  $AM_{18}$ , both the maximum amount of adsorbed herbicide ( $x_m$ ) and its

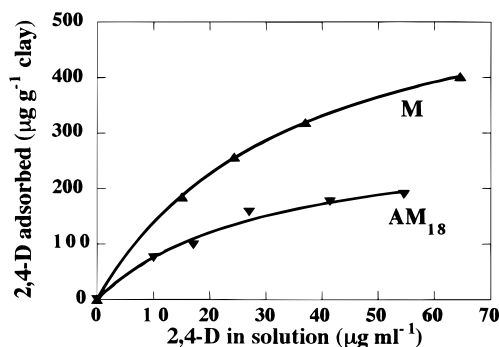


Fig. 3. Adsorption isotherms of 2,4-D at  $25^\circ\text{C}$  and pH 5.6 in 0.01 M phosphate buffer on montmorillonite and  $AM_{18}$ .

binding energy ( $k$ ) significantly decreased from 1052.8 to  $300 \mu\text{g g}^{-1}$  clay and from 1.35 to 0.03, respectively, if compared to those measured in acetate buffer (Fig. 4).

Herbicide desorption was not influenced by the nature of desorbing solution. Similar amounts of 2,4-D were removed by a 2,4-D- $AM_{18}$  complex by washing it with  $\text{CaCl}_2$  or acetate buffer solution.

Table 3 reports the desorption of 2,4-D from two 2,4-D- $AM_{18}$  complexes containing 651 and  $1000 \mu\text{g}$  of adsorbed herbicide  $\text{g}^{-1}$   $AM_{18}$ . A large amount of 2,4-D was removed immediately with the first washing (mixing time = 0 h) and only slightly more was removed by increasing the exposure time between herbicide- $AM_{18}$  complex and washing solution. After 24 h contact, 271 and  $378 \mu\text{g g}^{-1}$  complex, corresponding to 42 and 38%

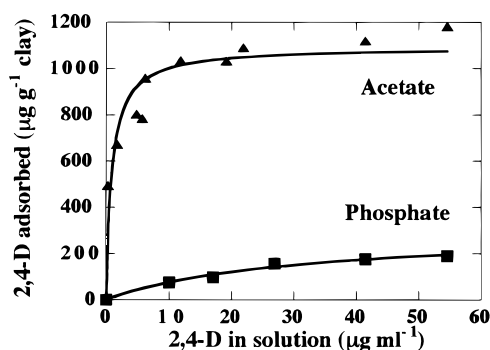


Fig. 4. Adsorption isotherms of 2,4-D on  $AM_{18}$  at  $25^\circ\text{C}$  and pH 5.6.

TABLE 2  
Langmuir and Freundlich Parameters for the Adsorption of 2,4-D by Clay Minerals (at  $25^\circ\text{C}$  and pH 5.6 in 0.01 M Acetate Buffer)

Complex	Langmuir equation			Freundlich equation			$K_d^b$ ( $\text{ml g}^{-1}$ )
	$x_m$	$k$	$r^{2a}$	$K$	$n$	$r^{2a}$	
M	—	—	—	—	—	—	—
$AM_3$	347.9	0.15	0.97	108.4	3.31	0.91	9.87
$AM_9$	512.8	0.44	1.00	290.0	4.21	1.00	16.07
$AM_{18}$	1052.8	1.35	0.92	611.3	5.48	0.90	35.32

<sup>a</sup> Correlation coefficients.

<sup>b</sup> Distribution coefficients.

TABLE 3

Kinetics of 2,4-D Desorption from 2,4-D-AM<sub>18</sub> Complexes Containing Different Amounts of the Herbicide

Time (h)	Amount desorbed ( $\mu\text{g g}^{-1}$ )		Desorption (%)	
	1 <sup>a</sup>	2 <sup>b</sup>	1 <sup>a</sup>	2 <sup>b</sup>
0	252	277	39	28
1	248	352	38	35
3	275	370	42	37
5	275	378	42	38
24	271	378	42	38

<sup>a</sup> 651  $\mu\text{g}$  of 2,4-D adsorbed  $\text{g}^{-1}$  AM<sub>18</sub>.<sup>b</sup> 1000  $\mu\text{g}$  of 2,4-D adsorbed  $\text{g}^{-1}$  AM<sub>18</sub>.

of the herbicide initially adsorbed, were desorbed from the two complexes, respectively.

It is also interesting to point out that desorption for the complex loading the lower quantity of herbicide did not change with the washing time. By contrast, 2,4-D removed from the complex loading the greater amount increased with the washing time and reached its maximum value after 5 h of exposure to the desorbing solution. Furthermore, when repeated washings lasting 5 h were performed on both the 2,4-D-clay complexes, no further desorption was measured at second and third washings. These results seem to indicate that some 2,4-D molecules desorb immediately from the complexes, whereas others are removed more slowly, probably because they are more strongly sorbed to the clay.

#### 4 DISCUSSION

The 2,4-D adsorption kinetics indicates that the process implies two kinds of retention, a fast one followed by slow one (Fig. 1). It could be presumed that the latter is a diffusion-controlled process.<sup>23</sup> To verify this assumption the adsorbed amounts were plotted versus square root of time (data not shown). The linear segment, observed after about 10 h of adsorption, might account for a diffusion-controlled process, thus supporting the assumption previously advanced.

The charge characteristics of clay minerals as well as the nature of buffers (acetate or phosphate) strongly affected the adsorption of 2,4-D on clays.

The absence of adsorption, observed on montmorillonite in acetate buffer, is strictly consistent with the results widely reported in the literature.<sup>7,20,21,24</sup>

Weber *et al.*<sup>7</sup> and Madrid *et al.*<sup>20</sup> demonstrated that a negative adsorption on montmorillonite surfaces occurred at pH values higher than the  $\text{pK}_a$  of the herbicide ( $\text{pK}_a$  2.80). The authors explained their results by a preferential adsorption of water with a concomitant exclusion of 2,4-D anions on the negatively charged surfaces of montmorillonite. Frissel<sup>21</sup> and Bailey *et al.*<sup>24</sup>

demonstrated that several acidic compounds gave rise to a negative adsorption on montmorillonite at pH values where the acids were in the dissociated form. A positive adsorption occurred when the pH of the bulk solution was about 1 to 1.5 units above the  $\text{pK}_a$  values.

At pH 5.6, 2,4-D is predominantly in the anionic form and is expected to be repelled by the negatively charged surfaces of montmorillonite.

The shapes of adsorption isotherms (Fig. 2) and the values summarised in Table 1 clearly indicate that the coating of montmorillonite with  $\text{Al}(\text{OH})_x$  species strongly and positively influenced 2,4-D adsorption. The larger the OH-Al loading on clay surfaces, the greater the quantity of 2,4-D adsorbed, the binding energy and the distribution coefficient.

The amounts of 2,4-D adsorbed on  $\text{Al}(\text{OH})_x$ -montmorillonite complexes were related to the quantities of OH-Al species coating the surfaces of montmorillonite rather than to the surface areas of clays. If reference is made to amounts of 2,4-D sorbed per gram of complex (Table 2) or per  $\text{m}^2$  of clay, the quantity of pesticide sorbed on AM<sub>18</sub> was 2.1 and 2.9 or 3.7 and 10 times greater than that fixed on AM<sub>9</sub> and AM<sub>3</sub>, respectively. Clearly, the OH-Al species tremendously promoted the sorption of anions.

The different capabilities of  $\text{Al}(\text{OH})_x$ -montmorillonite complexes to adsorb the herbicide seem to suggest that electrostatic interactions between the positive sites on clays, ascribable to the presence of  $\text{Al}(\text{OH})_x$  species, and 2,4-D predominated in the adsorption process. At pH 5.6, 2,4-D exists as an anion whereas AM<sub>18</sub> is the most positively charged complex. Further experiments made at a pH near the  $\text{pK}_a$  of 2,4-D demonstrated that the herbicide adsorbed at very low amounts on AM<sub>18</sub>, thus leading to the conclusion that the interaction between the supports and 2,4-D was substantially controlled by the pH.

According to the model proposed by Watson *et al.*,<sup>8</sup> 2,4-D molecules would be adsorbed with their  $\text{COO}^-$  groups oriented towards the positively charged surface of the clay. In such an arrangement, two types of adsorption might be postulated: a physical adsorption mediated by coulombic forces and a chemi-adsorption through a ligand exchange mechanism. The negative  $\text{COO}^-$  moieties of 2,4-D could not only interact with the positive  $\text{Al}(\text{OH})^{2+}$  groups on the clay surface through electrostatic interactions, but also exchange with  $-\text{OH}$  or water at the clay surface and create a bridge with two adjacent surface aluminium atoms.

This simplified model seems to be corroborated by the results obtained in phosphate buffer and in desorption experiments.

The amount of adsorbed pesticide and its affinity for the adsorbent considerably decreased in phosphate buffer (Fig. 4). Probably, phosphate and 2,4-D anions strongly competed for adsorption sites of chlorite-like complexes. Phosphate anions have a very high affinity

for aluminium species on which they are strongly sorbed, whereas acetate shows only a moderate affinity for aluminium. For these reasons, phosphate may compete with 2,4-D for sorption sites of  $\text{Al}(\text{OH})_x$ -montmorillonite complexes much more strongly than acetate, thus preventing 2,4-D sorption. As a consequence, several sorption sites were preferentially occupied by phosphate and were not available for interacting with 2,4-D anions.

Weber *et al.*<sup>7</sup> reported that the adsorption of 2,4-D on an anion-exchange resin was considerably decreased when phosphate anions from the 0.25 M phosphate buffer were present. They claimed that phosphate anions competed with 2,4-D anions for the positively charged sites on adsorbing supports.

In several studies, Violante and co-authors<sup>25-27</sup> have demonstrated that phosphate anions present a high affinity for the positively charged sites on the surfaces of chlorite-like complexes, thus strongly competing with many organic molecules for adsorption on such minerals. The presence of phosphate decreased more than five times the sorption of 2,4-D on the  $\text{AM}_{18}$  complex (Fig. 4).

Desorption experiments demonstrated that a large part (30–40%) of initially fixed 2,4-D was easily desorbable, evidently being only weakly bound to the support. Conversely, the remaining part was not removed from the complex, even after repeated washings or prolonged washing times (Table 3). On the basis of adsorption mechanisms proposed before, physically adsorbed herbicide molecules would be easily removed from the clay, whereas those bridged *via* the  $\text{COO}^-$  groups would be more strongly retained on the clay surface.

The adsorption of the herbicide on montmorillonite in phosphate buffer is not easily explicable. At pH 5.6, and independently of the nature of the buffer, both montmorillonite surfaces and the herbicide are negatively charged. Hence, neither electrostatic interactions nor ligand exchange bondings can establish between 2,4-D and clay. However, it could be hypothesised that magnesium and calcium ions, present as impurities in the clay, precipitate together with phosphate anions to form Mg or Ca phosphates, which collect on montmorillonite surfaces. Therefore, positive sites available for attracting 2,4-D anions are created. This hypothesis was confirmed by negative 2,4-D adsorption observed at the same pH and in phosphate buffer with a montmorillonite sample, lacking Ca and Mg impurities.

## 5 CONCLUSIONS

The results discussed in the present paper indicate that two factors governed and controlled the adsorption of 2,4-D on clays: (i) adsorbent-adsorbate interactions, and (ii) adsorbent-solvent interactions. With acetate buffer as the solvent, the herbicide was attracted suffi-

ciently to the positively charged surfaces of the chlorite-like complexes (electrostatic and ligand exchange mechanisms) to create a significant adsorption. With phosphate as the buffer, the adsorbent-phosphate interactions were strong enough to hinder partially the adsorption of the herbicide.

In the case of montmorillonite, a completely opposite situation occurred. In acetate buffer, the negative charges present on both clay surfaces and herbicide molecules prevented any kind of interaction between adsorbent and adsorbate. On the other hand, in phosphate buffer the possible reaction of phosphate anions with positive ions contained as impurities in the clays created potential positive sites and a measurable adsorption of the herbicide occurred.

Finally, a considerable part of adsorbed herbicide was firmly sorbed to  $\text{Al}(\text{OH})_x$ -montmorillonite complexes, thus constituting a fraction which can be referred to as the bound residue. In this aspect, chlorite-like complexes might be regarded as a 'sink' for 2,4-D in soils.

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## REFERENCES

1. Adams, R. S. Jr, Factors influencing soil adsorption and bioactivity of pesticides. *Res. Rev.*, **47** (1973) 1–54.
2. Bailey, G. W. & White, J. L., Factors influencing the adsorption, desorption and movement of pesticides in soil. *Res. Rev.*, **32** (1970) 29–92.
3. Hermosin, M. C. & Cornejo, J., Binding mechanism of 2,4-Dichlorophenoxyacetic acid by organo-clays. *J. Environ. Qual.*, **22** (1993) 325–31.
4. Boyd, S. A., Mortland, M. M. & Chiou, C. C., Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. *Soil Sci. Soc. Am. J.*, **52** (1988) 652–7.
5. Violante, A. & Huang, P. M., Influence of inorganic and organic ligands on the formation of aluminium hydroxides and oxyhydroxides. *Clays & Clay Min.*, **33** (1985) 181–92.
6. Frissel, M. J. & Bolt, G. H., Interaction between certain ionizable organic compounds (herbicides) and clay minerals. *Soil Sci.*, **94** (1962) 284–91.
7. Weber, J. B., Perry, P. W. & Upchurch, R. P., The influence of temperature and time on the adsorption of paraquat, diquat, 2,4-D and prometon by clays, charcoal and an anion-exchange resin. *Soil Sci. Soc. Am. Proc.*, **29** (1965) 678–88.
8. Watson, J. R., Posner, A. M. & Quirk, J. P., Adsorption of the herbicide 2,4-D on goethite. *J. Soil Sci.*, **24** (1973) 503–11.
9. Kavanagh, B. V., Posner, A. M. & Quirk, J. P., Effect of adsorption of phenoxyacetic acid herbicides on the surface charge of goethite. *J. Soil Sci.*, **31** (1980) 33–9.

10. Piccolo, A., Relationship between humic substances and organic pollutants in the environment. In *Humic substances in the global environment and implications on human health*, ed. N. Senesi & T. Miano. Elsevier, Amsterdam, 1994, pp. 961–80.
11. Boyd, S., Adsorption of substituted phenols by soil. *Soil Sci.*, **134** (1982) 337–43.
12. Scott, H. D., Wolf, D. C. & Lavy, T. L., Apparent adsorption and microbial degradation of phenol by soil. *J. Environ. Qual.*, **11** (1982) 107–12.
13. Barnishel, R. I. & Bertsch, P. M., Chlorites and hydroxy interlayered vermiculite and smectite. In *Minerals in Soil Environments*, ed. J. B. Dixon & S. B. Weed. Soil Science Society of America, Madison, Wisc., USA, 1989, pp. 729–78.
14. Huang, P. M., Role of soil minerals in transformations of natural organics and xenobiotics in soil. In *Soil Biochemistry*, Vol. 6, ed. J.-M., Bollag & G. Stotzky. Marcel Dekker, Inc., New York, 1990, pp. 29–115.
15. Jackson, M. L., *Soil Chemical Analysis—Advanced Course*, 2nd edn. M. L. Jackson, Madison, Wisconsin, 1979, pp. 100–66.
16. Peech, M., Cowan, R. L. & Baker, J. H., A critical study of the BaCl<sub>2</sub>-triethanolamine and ammonium acetate methods for determining the exchangeable hydrogen content of soils. *Soil Sci. Soc. Am. Proc.*, **26** (1962) 37–40.
17. Carter, D. L., Mortland, M. M. & Kemper, W. D., Specific surface. In *Methods of Soil Analysis, Part I. Physical and Mineralogical Methods*, ed. A. Klute. Soil Science Society of America, Madison, Wisc., USA, 1986, pp. 413–23.
18. Oh, K. H. & Tuovinen, O. H., Degradation of 2,4-dichlorophenoxyacetic acid by mixed cultures of bacteria. *J. Ind. Microbiol.*, **6** (1990) 275–8.
19. Bolth, G. H., & Warkentin, B. P., The negative adsorption of anions by clay suspensions. *Kolloid Zeitschrift*, **156** (1958) 41–6.
20. Madrid, L., Morillo, E. & Diaz-Barrientos, E., Competitive adsorption of 2,4-D and phosphate in soils. *Proc. Int. 3rd Workshop on Study of Pesticides Behaviour in Soils, Plants and Aquatic Systems*. GSF-Institut für Ökologische Chemie Munich-Neuherberg, 1990, 80–9.
21. Frissel, M. J., The adsorption of some organic compounds, especially herbicides, on clay minerals. *Versl. Land-bouwk. Onderz N.R.* (1961) 673-Wageningen.
22. Giles, C. H., Smith, D. & Huitson, A., A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *J. Coll. Interf. Sci.*, **47** (1974) 755–65.
23. Hamaker, J. W. & Thompson, J. M. In *Organic Chemicals in the Soil Environment*, Vol. 1. Marcel Dekker, New York, 1972, pp. 49–143.
24. Bailey, G. W., White, J. L. & Rothberg, T., Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. *Soil Sci. Soc. Am. Proc.*, **32** (1968) 222–34.
25. Violante, A., Colombo, C. & Buondonno, A., Competitive adsorption of phosphate and oxalate by aluminium oxides. *Soil Sci. Soc. Am. J.*, **55** (1991) 65–70.
26. Violante, A. & Gianfreda, L., Competition in adsorption between phosphate and oxalate on an aluminum hydroxide montmorillonite complex. *Soil Sci. Soc. Am. J.*, **57** (1993) 1235–41.
27. Violante, A., Rao, M. A., De Chiara, A. & Gianfreda, L., Sorption of phosphate and oxalate by a synthetic aluminium hydroxysulphate complex. *Eur. J. Soil Sci.*, **47** (1996) 241–7.